



A comparative study on the efficiency of electro-Fenton process in the removal of protham from water

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ABSTRACT

Electro-Fenton process has been widely used in the treatment of organic pollutants lately. Its oxidation efficiency mainly depends on the electrode materials. In this study, boron doped diamond (BDD), carbon sponge (CS) and platinum (Pt) electrodes were used at four different configurations as anode and cathode. The oxidation efficiencies of BDD anode and CS cathode were investigated together for the first time in the electro-Fenton process. Protham was used as the model pollutant. The obtained results indicate that the decay rate of protham and the mineralization rate of protham aqueous solutions were highest in the case of BDD and CS electrodes as expected. The obtained mineralization current efficiency (MCE) value was 81% at 100 mA in the presence of 0.2 mM Fe^{3+} for 30 min electrolysis. The oxidative degradation intermediates of protham showed different accumulation characteristics in all configurations. The oxamic acid resisted to mineralization but it rapidly degraded in the presence of BDD anode.

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1. Introduction

Protham is a carbamate herbicide used for the control of weeds in alfalfa, clover, flax, lettuces, afflow, spinach, sugar beets and pees. It prevents cell division and acts on meristematic tissues. Moreover, it is an acetylcholinesterase inhibitor and at the same time it could be degraded into aniline metabolites which are more dangerous substances than the parent molecule [1]. The presence of this substance in surface water was reported [2]. On the other hand, the maximum allowed amount of this substance is $0.1 \mu\text{g L}^{-1}$ in water intended for human consumption according to the EU Directive 98/83 [3]. Therefore, the removal of this substance from aqueous solutions has great importance. Different treatment techniques such as activated carbon adsorption, chemical oxidation, biological degradation, etc. can be applied to the removal of protham from water [4]. But these classical processes are not generally efficient enough in the elimination of such kind of pollutants. For example, activated carbon adsorption involves phase transfer of pollutants without decomposition and thus induces another pollution problem. Chemical oxidation is unable to mineralize the persistent organic pollutants. Concerning the biological treatment, the main drawbacks are: non-efficiency

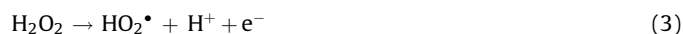
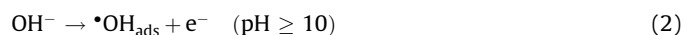
in presence of non-biodegradable and toxic pollutants, slow reaction rates, disposal of sludge and the need for strict control of proper pH and temperature. Up to now, some treatment processes different from the above mentioned classical methods such as membrane separation technique [5] and TiO_2 photocatalysis [6,7] were proposed in the literature. These processes have also some drawbacks; transportation of pollutants from one phase to another and formation of membrane fouling can be given as an example for membrane separation. TiO_2 photocatalysis suffers from low mineralization yields, high cost of light source and additional separation step for TiO_2 catalyst. In order to overcome these disadvantages, more powerful oxidation methods are required rather than those currently applied in wastewater treatments for achieving complete destruction of toxic and persistent pollutants.

Among these processes, the advanced oxidation processes (AOPs) have attracted great attention throughout the last two decades for the treatment of organic pollutants in aqueous solutions due to their ability which allows reaching the total mineralization [8–13]. These processes involve chemical, photochemical or electrochemical techniques to bring about chemical degradation of organic pollutants. The most widely used AOP is the Fenton's reaction. However, Fenton's reaction has some limitations in application such as the use of large quantities of chemical reagents, large production rates of ferric hydroxide sludge and slow catalysis of the ferrous ions generation [14,15]. Electrochemical AOPs overcome these drawbacks and offer many

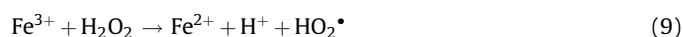
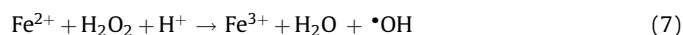
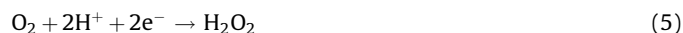
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advantages such as low operational cost and high mineralization degree of pollutants compared to other known chemical and photochemical ones. In this sense, anodic oxidation and electro-Fenton processes are very commonly used electrochemical AOPs.

In anodic oxidation, pollutants are mineralized by direct electron transfer reactions or action of radical species (i.e. hydroxyl radicals) formed on the electrode surface. In this manner, a wide variety of electrode materials have been investigated recently, but the boron doped diamond (BDD) has attracted great attention because of its high stability and efficiency [16–19]. This electrode allows to produce large quantities of hydroxyl radicals from water or hydroxide decomposition on the electrode surface (Eqs. (1) and (2)) [20–23]. The formation of H_2O_2 is also possible depending on the cathode materials used during the anodic oxidation process. The oxidation of formed H_2O_2 to HO_2^\bullet (Eq. (3)) and O_2 (Eq. (4)) takes place at anode surface [9]. The formed reactive species may react with the organics but their oxidation ability are poor compared to adsorbed $\bullet\text{OH}$ radicals.



In the electro-Fenton process, pollutants are destroyed by the action of Fenton's reagent in the bulk together with anodic oxidation at the anode surface. Fenton's reagent is formed in the electrolysis medium by the simultaneous electrochemical reduction of O_2 and Fe^{3+} to H_2O_2 (Eq. (5)) and Fe^{2+} (Eq. (6)) [24] respectively on the cathode surface. The reaction between these two species in the homogeneous medium allows the formation of $\bullet\text{OH}$ radicals (Eq. (7)) [25,26]. Eqs. (3) and (4) can also take place during the electro-Fenton process. Moreover, the oxidation of regenerated Fe^{2+} to Fe^{3+} may occur at the same time (Eq. (8)) on the anode surface. On the other hand, the existence of these reactions (Eqs. (3), (4) and (8)) is negligible compared to reaction (7) which occurs in the bulk because of the limited surface area of anode. Finally, iron species ($\text{Fe}^{3+}/\text{Fe}^{2+}$) can react with the formed reactive species from anodic and cathodic reactions (Eqs. (9)–(11)) [27]. The overall effect of these reactions influences the mineralization process of organics in the electro-Fenton treatment.



The $\bullet\text{OH}$ radicals formed by the procedures above illustrated are very powerful oxidizing agents. They react unselectively with organics giving dehydrogenated or hydroxylated by-products until their total conversion into CO_2 , water and inorganic ions. Because hydroxyl radical production does not involve the use of harmful chemical reagents which can be hazardous for the environment, electrochemical processes can be seen as environmentally friendly techniques. In conclusion, these processes seem to be very

promising for the purification of water polluted by persistent and/or toxic organic pollutants [8,13,24,25,28].

The efficiency of the electro-Fenton process mainly depends on the cathode material used in the electrolysis. On the other hand, the anode material has also a prominent effect on the process efficiency. In our previous studies, we used carbon sponge (CS) as a cathode in the electro-Fenton process [29] and BDD as an anode in the anodic oxidation process [19] to remove organic pollutants from water. These studies revealed that these electrodes are individually very effective in the generation of $\bullet\text{OH}$ radicals. In the light of these results, it can be concluded that combination of these two electrodes in the electro-Fenton process may increase the oxidation efficiency. The present study deals with the investigation of above tentative assumption. For this purpose, these two electrodes were used together for the first time in the electro-Fenton treatment of protham. Their efficiencies were also compared with that of Pt electrode as classical anode of electro-Fenton processes. The removal of protham from water and the mineralization of aqueous protham solutions were followed by high performance liquid chromatography (HPLC) and total organic carbon (TOC) analysis, respectively. The obtained results pointed out that the combination of BDD and CS electrodes as anode and cathode in the electro-Fenton process provides the most efficient configuration compared to other configurations tested in this study and those of the literature [19,30]. Another purpose of this study is to investigate the effects of electrode materials on the accumulation of the oxidation by-products of protham during the electro-Fenton process. The intermediates especially oxamic acid and ammonium displayed different accumulation characteristics in the case of the use of BDD or Pt anodes in the electro-Fenton processes.

2. Materials and methods

2.1. Materials

Protham was obtained from Riedel-de Haën. Sodium sulphate (anhydrous, 99%), sulphuric acid (ACS reagent grade, 98%) and acetic acid (glacial p.a.) were purchased from Across. Iron(III) sulphate pentahydrate (97%) and oxalic acid (98%) were obtained from Aldrich. Sodium nitrate (99%) and ammonium nitrate (99%) were obtained from Merck. Potassium sulphate (99%) and oxamic acid (96%) were purchased from Fluka. All solutions were prepared by using pre-distilled $18 \mu\text{S cm}^{-1}$ deionized water (Sartorius).

2.2. Procedures and equipment

Experiments were performed in a 0.175 L undivided cylindrical glass cell (internal diameter: 5.0 cm) equipped with two electrodes. The cell was surrounded by a water jacket and the temperature of the reaction medium was held at 35°C by water circulation with a water bath. BDD thin-film electrode which is deposited on both sides of a niobium substrate ($3.0 \text{ cm} \times 4.0 \text{ cm}$) was obtained from Magneto Chem and used as anode. CS ($1.0 \text{ cm} \times 1.0 \text{ cm} \times 4.0 \text{ cm}$) was purchased from Magneto BV Holland and used as cathode. A Pt grid ($3.0 \text{ cm} \times 4.0 \text{ cm}$) from Aldrich was used as anode and/or cathode. According to the used electrode configurations, electro-Fenton processes were denoted as BDD//Pt (BDD anode-Pt cathode), Pt//CS (Pt anode-CS cathode), Pt//Pt (Pt anode-Pt cathode) and BDD//CS (BDD anode-CS cathode). Prior to electrolysis, electrodes were cleaned by electrolyzing for 20 min in aqueous Na_2SO_4 (50 mM) solution. Experiments were performed in 0.15 L protham ($C_0 = 0.50 \text{ mM}$) aqueous solutions containing 0.05 M Na_2SO_4 or K_2SO_4 as supporting electrolyte. The pH of the medium was set to 3.0 by using 1.0 M H_2SO_4 . The applied current density values were 8.33 mA cm^{-2} (100 mA),

25.00 mA cm⁻² (300 mA) and 41.67 mA cm⁻² (500 mA). Reaction medium was agitated continuously by a magnetic stirrer (500 rpm). In the case of electro-Fenton experiments, a catalytic quantity of iron(III) sulphate pentahydrate (0.05, 0.1 and 0.25 mM) was introduced into the solution and compressed air was bubbled through the solution during electrolyses.

2.3. Analytical measurements

The prophan removal and evolutions of the aromatic intermediates were monitored by HPLC using an Agilent 1100 system equipped with a diode array detector and an autosampler. A reversed phase Inertsil ODS-3 (5-μm, 4.6-mm × 250-mm) column was used in the experiments. The column was thermostated at 40 °C. 20 μL samples were injected. The column was eluted with a mixture of water–methanol–acetic acid at 44:54:2 (v/v/v) with a flow rate of 0.9 mL min⁻¹. Detection was performed at 254 and 280 nm. Carboxylic acids were identified and quantified by a Supelcogel H column (φ = 7.8 mm × 300 mm) which was thermostated at 40 °C with a mobile phase of 4 mM H₂SO₄. The detection was performed at 210 nm.

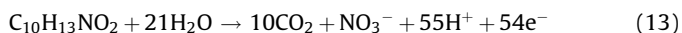
The concentrations of ammonium and nitrate ions released during the electrolysis were measured by ion chromatography (Dionex-100 equipped with a conductivity detector). A cationic exchanger column (IonPac[®] CS12A-Dionex) was used for ammonium ion and an anionic exchanger column (IonPac[®] AS14-Dionex) was used for nitrate ions. The volume of injections was 25 μL. The mobile phase and regenerant solution for the cationic column were 20 mM methanesulphonic acid (70%, Fluka) with a flow rate of 0.85 mL min⁻¹ and 100 mM tetrabutylammonium hydroxide (40%, Aldrich), respectively. On the other hand, 30 mM sodium hydroxide (99%, Fluka) with a flow rate of 0.80 mL min⁻¹ and 22 mM H₂SO₄ was used for the anionic column as mobile phase and regenerant, respectively. Calibration curves were obtained by using the pure standards of the related ions.

The TOC of the initial and electrolyzed samples was determined with a Shimadzu TOC-V analyzer. The platinum catalyst was used in the combustion reaction. The carrier gas was oxygen with a flow rate of 150 mL min⁻¹. A non-dispersive infra-red detector, NDIR, was used in the TOC system. Calibration of the analyzer was attained with potassium hydrogen phthalate (99.5%, Merck) and sodium hydrogen carbonate (99.7%, Riedel-de Haën) standards for total carbon (TC) and inorganic carbon (IC), respectively. The difference between TC and IC analysis gives TOC data of the sample.

The mineralization current efficiency (MCE) values were determined by using the following expression (Eq. (12)) [31]:

$$\text{MCE} = \frac{\Delta(\text{TOC})_{\text{exp}}}{\Delta(\text{TOC})_{\text{theor}}} \times 100 \quad (12)$$

$\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC at a given time and $\Delta(\text{TOC})_{\text{theor}}$ is the theoretical TOC removal considering the applied electrical charge (=current × time) consumed for the mineralization of prophan according to the following reaction which presupposes the consumption of 54 F mol⁻¹ of prophan (Eq. (13)):



3. Results and discussion

3.1. Comparative removal kinetics of prophan in the electro-Fenton process

The removal kinetics of prophan (C_0 : 0.5 mM) was investigated at constant current controlled conditions (100 mA) in the presence of 50 mM Na₂SO₄ and 0.2 mM Fe³⁺ for BDD//Pt, Pt//CS and BDD//CS

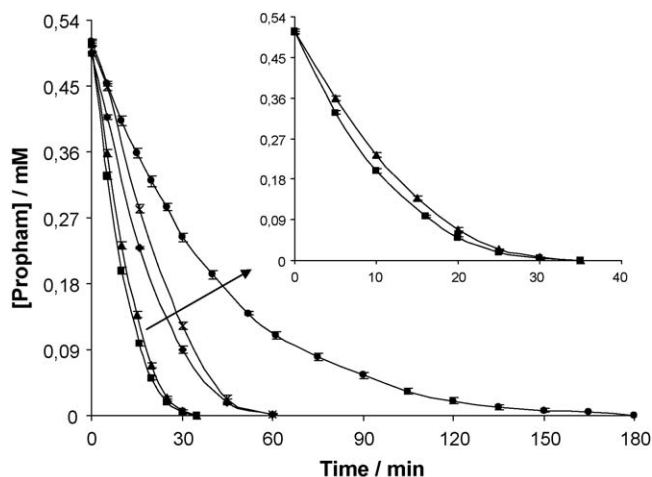


Fig. 1. Removal kinetics of prophan during the treatment by AO (○), BDD//Pt (◆), Pt//CS (▲), BDD//CS (■) and Pt//Pt (×) systems. C_0 : 0.5 mM, [Na₂SO₄]: 50 mM, I : 100 mA, V : 0.15 L, pH: 3.0, T : 35 °C. [Fe³⁺]: 0.2 mM.

systems in acidic media (pH 3). The removal of prophan in each process was monitored by HPLC analyses and the results are given in Fig. 1. The decay rate of prophan was higher in BDD//CS system than in BDD//Pt system. This result indicates that H₂O₂ production ability of CS was higher than that of Pt. A slight increase was observed in removal rate in the case of BDD//CS compared to Pt//CS system. The formation rate of hydroxyl radicals and the decay rate of organics are faster on BDD anode than that of Pt. These two effects increase the destruction rate of prophan in BDD//CS system. Hammami et al. [36] also reported similar results for BDD and Pt anodes in the electro-Fenton process which enhances our findings. To evaluate which process is dominant in the destruction of prophan in the case of BDD//Pt, experiments were repeated by the same cell in the absence of Fe³⁺ ions which is known as anodic oxidation (AO) process. The complete removal of prophan needed 180 min in AO whereas it is achieved in 60 min in the presence of Fe³⁺ ions. The electrochemical generation of H₂O₂ is possible during the AO process on the Pt cathode surface. H₂O₂ contributes to the oxidation process but its oxidation ability is very poor compared to •OH radicals. Therefore, the destruction rate of prophan was not so high in the absence of Fe³⁺ catalyst. Moreover, the experiments were performed at BDD//Pt conditions using Pt anode instead of BDD (Pt//Pt). The removal rate was slightly higher for BDD//Pt compared to Pt//Pt at the beginning of the electrolysis. The obtained results from last two experiments showed that the destruction of prophan was occurred mainly by the •OH radicals generated from Fenton's reaction. This result confirms that prophan removal is faster on BDD anode compared to Pt. However, the complete prophan removal was achieved at 60 min in both processes owing to mass transfer limitations at longer electrolysis times. These results confirm that the use of BDD as anode in the electro-Fenton process slightly increases the removal rate of prophan.

Our previous data showed that prophan removal follow a pseudo-first order reaction kinetic in electro-Fenton [30] and anodic oxidation [19] processes. The rate expression of prophan removal with hydroxyl radicals can be written as (Eq. (14)):

$$\frac{d[\text{Prophan}]}{dt} = k_{\text{abs}}[\bullet\text{OH}] \times [\text{Prophan}] = k_{\text{app}}[\text{Prophan}] \quad (14)$$

where k_{abs} and k_{app} are respectively the absolute and apparent rate constant of the reaction, supposing the quasi-steady-state assumption for •OH concentration. The apparent rate constant values were calculated by using the integrated forms of Eq. (8). The

Table 1

Apparent rate constant values for the oxidation of propham by BDD//CS system in the presence of different (a) applied current and (b) Fe^{3+} concentration values. C_0 : 0.5 mM, $[\text{Na}_2\text{SO}_4]$: 50 mM, V : 0.15 L, pH : 3.0, T : 35 °C. (a) $[\text{Fe}^{3+}]$: 0.2 mM. (b) I : 300 mA.

(a) Applied current (mA)	k_{app} (min^{-1})	R^2	(b) $[\text{Fe}^{3+}]$ (mM)	k_{app} (min^{-1})	R^2
100	0.0933	0.9938	0.1	0.0989	0.9917
300	0.1553	0.9937	0.2	0.1553	0.9937
500	0.0937	0.9995	0.5	0.1738	0.9918

obtained apparent rate constants in the presence of different applied current and Fe^{3+} concentration values for BDD//CS are given in Table 1. As can be seen, the apparent rate constant values increase with increasing applied current value from 100 to 300 mA. On the other hand, a prominent decrease was observed at 500 mA. The reasons of the propham removal decrease at high applied current (or potential) values can be explained by the competition of two parasitic reactions: (i) the 4- e^- reduction of O_2 leading to the formation of H_2O (Eq. (15)) which inhibits H_2O_2 formation reaction (Eq. (5)) on the CS cathode and (ii) the hydrogen evolution from H_2O reduction (Eq. (16)). However, the O_2 evolution is more favourable rather than $\cdot\text{OH}$ on the BDD anode at higher current values. Moreover, the formation of weak oxidant species such as persulphate ions (compared to $\cdot\text{OH}$) (Eq. (17)) is also possible. We previously reported that the decay rate of propham did not change significantly by the increase of applied current values from 30 to 500 mA with BDD anode [19] in anodic oxidation whereas it increased up to 300 mA in electro-Fenton process [30]. These results are in accordance with those obtained in this study.



In addition, the apparent rate constant values increased significantly by the increasing of Fe^{3+} concentration from 0.1 to 0.2 mM. Approximately the same apparent rate constant was observed in the case of 0.2 and 0.5 mM Fe^{3+} . After a certain value, an increase in the amount of Fe^{3+} concentration inhibits the removal rate of propham because of the waste reaction between Fe^{2+} and hydroxyl radicals (Eq. (18)) [32]. This result was reported many times in literature. Therefore, the optimal Fe^{3+} concentration was determined as 0.2 mM. In our previous study, this value was determined as 0.5 mM for the propham removal in the electro-Fenton process [30]. The combination of BDD and CS electrodes in the electro-Fenton process permitted to decrease 60% of optimal Fe^{3+} concentration. In agreement with these results, one can note that the apparent rate constant value (0.0933 min^{-1}) obtained at 100 mA in this study is three times higher than that of the literature value (0.0288 min^{-1}) obtained at the same experimental conditions [19]. This situation can be explained by the higher efficiencies of the BDD and CS electrodes.



3.2. Mineralization efficiency of propham

HPLC analysis indicated that propham concentration gradually decreased and the parent molecule (propham) was converted to more simple by-products during the electro-Fenton processes. The destruction of the propham does not constitute an indication of its complete mineralization during the treatment. Mineralization is equivalent of the complete conversion of initial organics to carbon dioxide and inorganic ions. As a result, mineralization ability of the

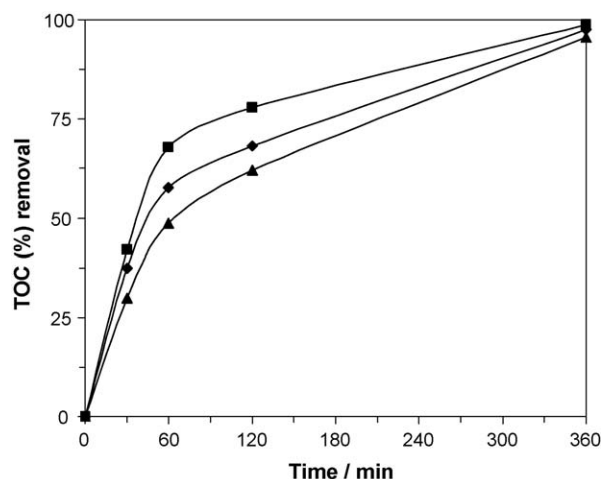


Fig. 2. TOC (%) removal values obtained during the treatment of propham by BDD//Pt (◆), Pt//CS (▲) and BDD//CS (■) systems. C_0 : 0.5 mM, $[\text{Na}_2\text{SO}_4]$: 50 mM, $[\text{Fe}^{3+}]$: 0.2 mM, I : 100 mA, V : 0.15 L, pH : 3.0, T : 35 °C. Initial TOC: $62.36 \text{ mg C L}^{-1}$.

process is very important in the treatment of toxic organic pollutants. To investigate the efficiencies of BDD//Pt, Pt//CS and BDD//CS, comparative experiments were carried out at the same conditions. The mineralization of aqueous propham solutions was monitored by measuring the TOC removal during the electrolysis. The mineralization of propham can be shown as follows (Eq. (19)):



The TOC (%) removal evolutions by three different electro-Fenton configurations were depicted in Fig. 2 in function of electrolysis time. As can be seen, there is a fast TOC removal at the initial stage of electrolysis until 1.5 h ($Q = 1.5 \text{ Ah L}^{-1}$) and then decreases gradually for all systems. The TOC removal efficiency is in the following order; Pt//CS < BDD//Pt < BDD//CS. A significant difference was observed between TOC removal rates in the first hour of electrolysis. While the removal rate of propham was faster in Pt//CS system than in BDD//Pt system (see Fig. 1), the TOC removal rate of propham was faster in BDD//Pt system. This unexpected result can be explained in the following way: While the decay rate of propham was very fast, the accumulation rates of aromatic intermediates were very high in the case of Pt//CS system. Therefore, the TOC removal rate of BDD//Pt system was higher than that of Pt//CS system. This result can be related to the higher oxidation power of BDD anode in the mineralization of carboxylic acids compared to the Pt anode. Since the BDD//CS system was the most effective process, we optimized the applied current and Fe^{3+} concentration values for this system. The evolution of TOC (%) removal values with treatment time is given in Fig. 3. As can be observed, the TOC removal rate increased with the increasing of applied current from 100 to 300 mA (Fig. 3a) and Fe^{3+} concentration from 0.1 to 0.5 mM (Fig. 3b). Almost 99% TOC removal was observed after 6 h treatment in all cases. Table 2 shows the TOC and corresponding MCE values of these experiments. The TOC removal rates increased and the MCE values decreased with the increasing of applied current. The MCE was 81% at 100 mA in the presence of 0.2 mM Fe^{3+} for 30 min electrolysis. This value is superior to that reported in literature values of 77% for anodic oxidation with BDD electrode [19] and 35% for electro-Fenton process with carbon felt cathode [30]. This result showed that the combination of BDD and CS electrodes in the electro-Fenton process are very effective for the mineralization of propham.

To compare the efficiency of BDD//Pt, Pt//CS and BDD//CS systems, the energy consumption (EC) values of these systems

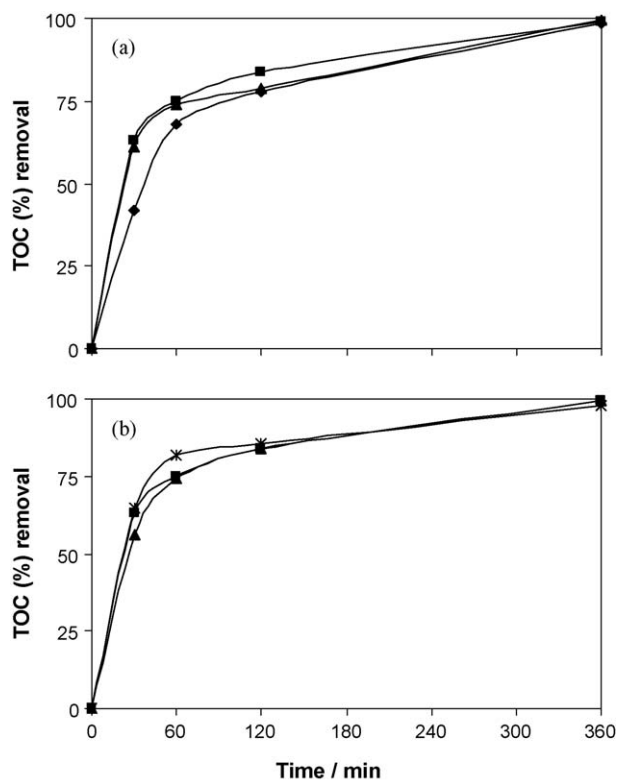


Fig. 3. TOC (%) removal values of BDD//CS system obtained at different applied current values (a) (◆: 100, ■: 300 and ▲: 500 mA) and Fe^{3+} concentrations (b) (▲: 0.1, ■: 0.2 and ✱: 0.5 mM). Initial TOC: $62.36 \text{ mg C L}^{-1}$, C_0 : 0.5 mM, $[\text{Na}_2\text{SO}_4]$: 50 mM, V : 0.15 L, pH: 3.0, T : 35°C . (a) $[\text{Fe}^{3+}]$: 0.2 mM, (b) I : 300 mA.

Table 2

Effects of (a) applied current and (b) Fe^{3+} concentration on the mineralization of prophan by BDD//CS system and corresponding MCE% values. C_0 : 0.5 mM, $[\text{Na}_2\text{SO}_4]$: 50 mM, V : 0.15 L, pH: 3.0, T : 35°C . (a) $[\text{Fe}^{3+}]$: 0.2 mM, (b) I : 300 mA.

Applied current (mA)		100	300	500	100	300	500
(a)		TOC (mg C L^{-1})			MCE (%)		
Time, min	30	36.1	23.1	24.2	81	40	24
	60	20.1	15.7	16.4	65	24	14
	120	13.8	10.0	13.1	37	13	8
	360	0.8	0.5	0.3	16	5	3
$[\text{Fe}^{3+}]$ (mM)		0.1	0.2	0.5	0.1	0.2	0.5
(b)		TOC (mg C L^{-1})			MCE (%)		
Time, min	30	27.2	23.1	22.1	36	40	42
	60	16.0	15.7	11.3	24	24	26
	120	10.1	10.0	8.9	13	13	14
	360	0.4	0.5	1.3	5	5	5
-Initial TOC : $62.36 \text{ mg C L}^{-1}$							
-MCE (%) values calculated from Eq. 6.							

Initial TOC: 62.3 mg C L^{-1} . MCE (%) values calculated from Eq. (6).

were calculated for the experimental results of Fig. 2 according to the following equation [33].

$$\text{EC (kWh m}^{-3}\text{)} = \left[\frac{V(V) \times I(A) \times t(h)}{V(L)} \right] \times \left[\frac{\text{TOC}_{\text{in}}}{\Delta\text{TOC}_{\text{exp}}} \right] \quad (20)$$

where V and I are the observed potential and the applied current values, respectively. V is the volume of the treated solution. TOC_{in} shows the initial TOC and $\Delta\text{TOC}_{\text{exp}}$ illustrates removed TOC values at a given time. The EC values of BDD//Pt, Pt//CS and BDD//CS systems were calculated as 6.02, 5.75 and 4.72 kWh m^{-3} , respectively, for the first hour of electrolysis. These results revealed that BDD//CS system was the most energy effective system.

3.3. Evolution of prophan oxidation intermediates

3.3.1. Aromatic intermediates

The oxidation of prophan leads to the formation of several aromatic by-products during the electro-Fenton process. Some of them were determined in our previous study [30]. Here, the most

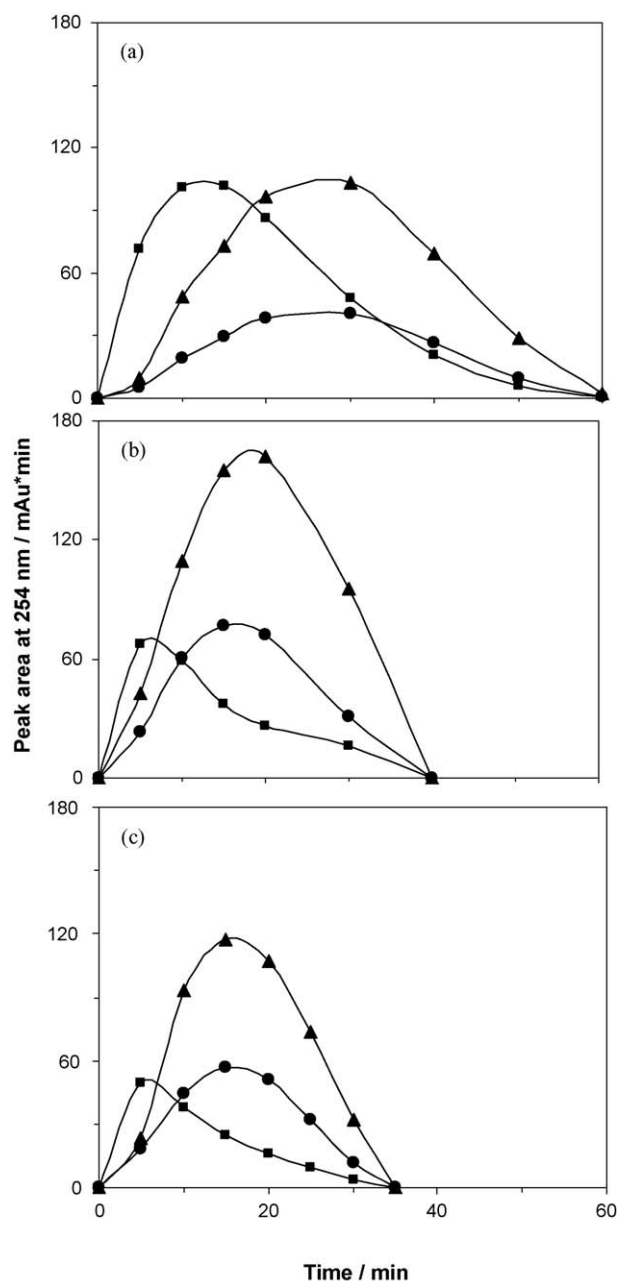


Fig. 4. Evolution of benzoquinone (■), p-hydroxyprophan (▲) and o-hydroxyprophan (●) during the treatment of 0.5 mM prophan by the BDD//Pt (a), Pt//CS (b) and BDD//CS (c) systems. $[\text{Na}_2\text{SO}_4]$: 50 mM, $[\text{Fe}^{3+}]$: 0.2 mM, I : 100 mA, V : 0.15 L, pH: 3.0, T : 35°C .

dominant three intermediates (o-hydroxypropham, p-hydroxypropham and benzoquinone) were chosen to investigate the effects of electrode materials on their accumulation in the reaction medium. Their evolutions were followed by HPLC analysis (Fig. 4). The amounts of accumulated o- and p-hydroxypropham reached their maximal values at almost 30 min and their complete destruction needed 60 min in BDD//Pt system (Fig. 4a). On the other hand, the required maximal accumulation times for these intermediates were 20 and 15 min for Pt//CS (Fig. 4b) and BDD//CS (Fig. 4c) systems, respectively. In our previous study, it was observed that the accumulation of o-hydroxypropham was very low during the anodic oxidation [19] whereas it was quite high during the electro-Fenton [30] treatment. The obtained results in this study are in agreement with those of the literature cited. The results explain why the TOC removal values of Pt//CS system are lower than that of BDD//Pt and BDD//CS systems in the first 30 min. These results also indicate that accumulation of these intermediates is very low in the presence of BDD electrode.

3.3.2. Short-chain carboxylic acids

The oxidative ring opening reactions of hydroxylated aromatic (or quinoid) intermediates allow the formation of short-chain carboxylic acids during the electro-Fenton treatment [12,34,35]. Oxalic, oxamic, acetic, formic, maleic, fumaric and glyoxylic acids were observed previously during the anodic oxidation [19] and electro-Fenton [30] treatments of propham. In this study, almost the same carboxylic acids were observed during the BDD//Pt, Pt//CS and BDD//CS treatments. To compare the accumulation behaviour of carboxylic acids in these three systems, two dominant carboxylic acids, oxalic and oxamic acids, were chosen and their evolutions were given in Fig. 5. As can be seen, their formation rates are very fast at the initial stage of the electrolysis for all

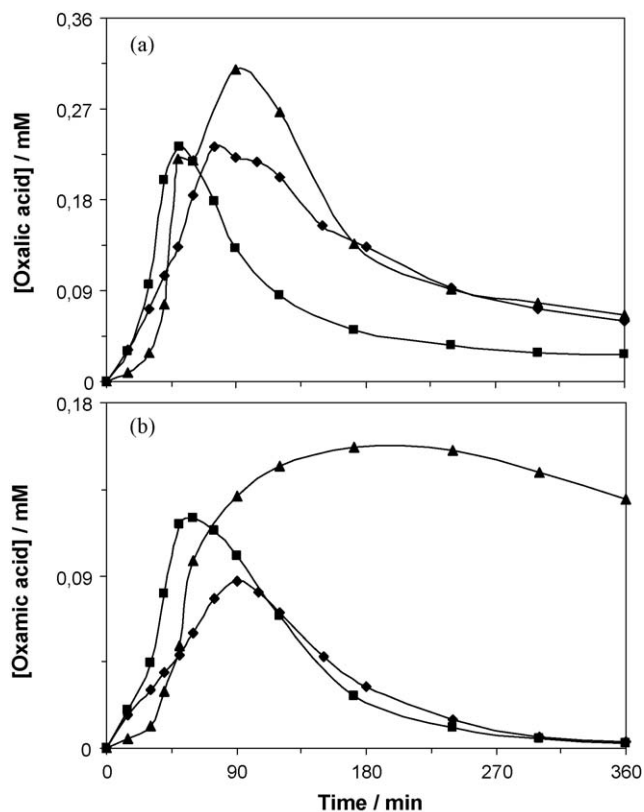


Fig. 5. Evolutions of oxalic (a) and oxamic (b) acids during treatment of propham by BDD//Pt (◆), Pt//CS (▲) and BDD//CS (■) systems. C_0 : 0.5 mM, $[\text{Na}_2\text{SO}_4]$: 50 mM, $[\text{Fe}^{3+}]$: 0.2 mM, I : 100 mA, V : 0.15 L, pH: 3.0, T : 35 °C.

systems but their relative formation and decay rates can be classified as BDD//CS > BDD//Pt > Pt//CS. They reached their maximal values less than 60 and 80 min in BDD//CS and in BDD//Pt systems, respectively. On the other hand, the maximal accumulation values of oxalic and oxamic acids were observed at 100 and 180 min respectively in Pt//CS system. Although the decay rate of oxamic acid was very high in BDD//Pt and BDD//CS systems, it was very low in Pt//CS system. This situation may be explained by higher oxidation rate of oxamic acid at BDD anode surface. Another reason may be the formation of reactive species (persulphate ions) on the BDD anode (Eq. (17)) which can oxidize this acid. The high accumulation levels of these carboxylic acids in Pt//CS system bring also an explanation to low TOC removal rate of Pt//CS system. In conclusion, the use of BDD electrode as an anode is very important for the degradation of oxamic acid in order to reach a complete mineralization quickly.

3.3.3. Inorganic ions

The heteroatoms in organics are converted to inorganic species during the oxidation process. The formations of ammonium and nitrate ions were observed during the electro-Fenton treatment of propham [28]. The evolution of these species was followed by ion

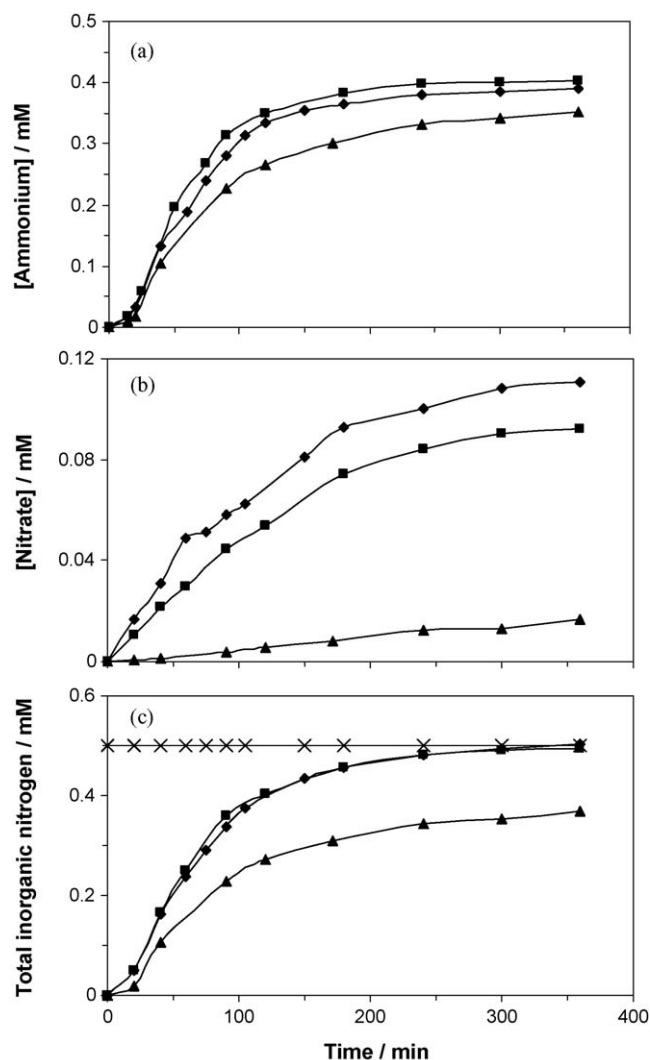


Fig. 6. Evolutions of ammonium (a), nitrate (b) and total inorganic nitrogen (c) during the treatment of propham by BDD//Pt (◆), Pt//CS (▲) and BDD//CS (■) systems. (x) represent the theoretical value of the initial nitrogen. C_0 : 0.5 mM, $[\text{Na}_2\text{SO}_4]$: 50 mM, $[\text{Fe}^{3+}]$: 0.2 mM, I : 100 mA, V : 0.15 L, pH: 3.0, T : 35 °C.

chromatography during the BDD//Pt, Pt//CS and BDD//CS systems and comparative results are given in Fig. 6. It can be figured out that most of the initial nitrogen was converted to ammonium ions in all systems. Accumulation of ammonium and nitrate ions were very fast in the first hour, after that time, accumulation rate gradually decreased and reached to a steady-state value in each case. Ammonium accumulation was the highest in BDD//CS system (Fig. 6a), whereas nitrate accumulation was the highest in BDD//Pt system (Fig. 6b). This situation may arise from the observed potential difference between these two systems. The potential values were 4.8 and 5.2 V for BDD//CS and BDD//Pt systems, respectively. This difference may stem from the large surface area of CS electrode according to the Pt. The total amount of ammonium and nitrate ions reached to initial stoichiometric value of nitrogen (C_0 : 0.5 mM) in BDD//Pt and BDD//CS systems (Fig. 6c). However, this result was not observed in Pt//CS system because some nitrogen atoms were found as oxamic acid (~ 0.13 mM) in the solution. It can be easily seen in Fig. 5b.

4. Conclusions

The decay kinetics and mineralization of protham were investigated by using BDD, CS and Pt electrodes as anode and/or cathode at four different configurations in the electro-Fenton process. The mineralization efficiency of different electro-Fenton process configurations investigated is related with the electrode materials. The best results were obtained in the case of CS cathode and BDD anode. The highest TOC removal efficiency and the lowest MCE values were observed at 500 mA in the presence of 0.2 mM Fe^{3+} . The best MCE value of 81% was obtained at 100 mA in the presence of 0.2 mM Fe^{3+} for 30 min treatment. This value is superior to that reported in our previous studies using different electrode combinations [19,30]. The main oxidation intermediates were determined as benzoquinone, o- and p-hydroxyprotham and short-chain carboxylic acids such as oxamic and oxalic acid. Nitrogen presented in protham was almost quantitatively released into the solution in ammonium and nitrate forms. Aromatic intermediates were poorly accumulated during treatment with BDD//CS system. The BDD anode has also a significant effect on the mineralization rate of carboxylic acids.

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